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(FINAL REPORT)

INTERACTION OF GASES WITH LUNAR MATERIALS

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Contents

The progress report for this period consists of the preprints of three papers.

1. R. B. Gammage and H. F. Holmes, "Alteration of Apollo 17 Orange Fines by Adsorbed Water Vapor," submitted for publication in J. Coll. Interfac. Sci.
2. H. F. Holmes and R. B. Gammage, "Interaction of Gases with Lunar Materials: Revised Results for Apollo 11," submitted for publication in Proc. Sixth Lunar Sci. Conf.
3. R. B. Gammage and H. F. Holmes, "Blocking of the Water-Lunar Fines Reaction by Air and Water Concentration Effects," submitted for publication in Proc. Sixth Lunar Sci. Conf.

ALTERATION OF APOLLO 17 ORANGE FINES  
BY ADSORBED WATER VAPOR\*

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ABSTRACT

The Apollo 17 orange fines have a unique character and history. The changes in surface properties induced by adsorbed water vapor are evaluated and compared to those produced in soil samples from other locations, including an immediately adjacent Apollo 17 grey soil.

Adsorbed water vapor changes the condition of each sample of fines from non-porous to porous. Particle size distributions show that the changes are internal to the particles. The data from t-plots, the fractional areas contained within micropores, the amounts of irreversibly adsorbed water held within the pores and the blocking action of this water on subsequently adsorbed nitrogen, all show the interconnecting channels in the orange fines to be wider than is general for other types of fines.

Our interpretation is that leaching by water of material within radiation damage tracks has widened channels to the point where few micro-sized pores remain and the accessibility of the pore system is greater than usual. The high reactivity of the orange fines is considered in light of damage caused by heavy cosmic ray nuclei and the unusually high content of halogens which might provide for stronger than usual etching conditions upon exposure to water vapor.

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## INTRODUCTION

Lunar soils or fines from different locations on the moon's surface are rather similar with respect to their reactivity towards water vapor (1, 2, 3). This is remarkable when one takes into account different chemical compositions and exposures to solar and galactic radiations. This report is concerned primarily with the orange colored soil (74220) and an adjacent light grey colored soil (74241) collected during the Apollo 17 mission from the rim of the Shorty Crater. The results of water vapor sorption are especially significant because they show deviations from the norm and because the physical characteristics of the orange soil are unique (see this section). Also water is considered by us (4) to be a mild etching agent (for the etching of damage tracks). If this is true the manner in which the orange fines are attacked has significance for the findings of those workers engaged in track etching studies (5-12). History (13,14).

The orange soil (74220) was formed  $3.7 \times 10^9$  years ago, in conjunction with the local mare basalt, probably through the action of volcanic fire fountains. These produced large amounts of melted rock in the form of tiny droplets which cooled rapidly. All the spheres and broken droplets have nearly the same chemical composition of 39%  $\text{SiO}_2$ , 22%  $\text{FeO}$ , 14%  $\text{MgO}$ , 9%  $\text{TiO}_2$ , 8%  $\text{CaO}$ , 6%  $\text{Al}_2\text{O}_3$ , 1%  $\text{Cr}_2\text{O}_3$  and <1%  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  (15). The smallest particles are clear orange glass fragments. The larger particles, which cooled the slowest, had a chance to recrystallize partially or completely and as a result contain plates of olivine or ilmenite. The mean grain size is 40  $\mu\text{m}$  (16).

The orange color does not imply oxidation, rather the color of these lunar glasses results from the interaction of crystal-field and charge-transfer absorption bands of iron and titanium which reflect the high titanium and iron content of the underlying bedrock. Glasses of this type have, in fact, been found in soils from every site visited on the moon but never in such high concentrations.

The orange soil was covered over shortly after its formation to be exhumed only recently ( $10$  to  $30 \times 10^6$  years ago) by the impact which produced Shorty Crater. The orange soil which was sampled formed a layer 80 cm wide and 25 cm deep flanked by light grey material (74241) and underlain by black soil (74001).

The orange glass is also unique with respect to its radiation exposure history. In spite of its great age it has suffered minimal exposure to solar wind and flare particles (sampling was done at a depth of 5 to 7.5 cm). The damage tracks ( $10^6/\text{cm}^2$ ) are dominantly from penetrating, heavy cosmic ray nuclei. The spherules also contain a background of uranium fission tracks ( $10^5/\text{cm}^2$ ). They contain only 1/100 of the trapped hydrogen found in the control soil (74241) which is a very gas-rich surface soil (17), like Apollo 16 (63341) and 12 (12070) soils which are also used for comparative purposes in this study.

The orange soil presents a contrasting subject to the mature surface fines we have studied previously in gas adsorption measurements where the micron sized grains are usually severely radiation damaged as a result of which they possess an amorphous coating (500-1000 Å) rich in solar wind ( $0.1 - 1.0 \text{ cm}^3 \text{ H}_2$  (STP)/g) and damage tracks in

in excess of  $10^{11}/\text{cm}^2$  (12). Another difference is that the orange fines, unlike most other mature surface soils, have not been subjected, extensively to the fining action of micrometeorite impacts.

#### EXPERIMENTAL

Vacuum microbalance systems were used, as before (1,2,3), for making adsorption measurements. Great care was exercised in the application of background and buoyancy corrections (1) the magnitudes of which are often greater than the weight of adsorbed gas.

The ~~two~~ fines samples had been processed and stored in an atmosphere of dry nitrogen. During the procedure of weighing and loading onto the balance, the fines suffered an unavoidable exposure to air for about one hour.

The fines particles were spread as a dry powder, on Scotch tape in order to observe their shape and size characteristics in a scanning electron microscope.

#### RESULTS

##### Particle Shapes and Sizes

Scanning electron micrographs were taken, at 500 and 10,000 magnifications, of the orange fines 74220 both before and after the attack by adsorbed water vapor. The frequency with which particles occur in the sub-micron and micron size ranges are listed in Table 1. The appearance of the orange glass spheroids, shards and attached debris is shown in Fig. 1; at these magnifications no changes can be detected as a result of the attack by water vapor.

### Isotherms of Nitrogen and t-Plots

The complete isotherms of nitrogen, argon, oxygen and water vapor for adsorption on the Apollo 17 orange and adjacent grey fines are published separately<sup>(3)</sup>. Presented here in Fig. 2 are the nitrogen isotherms measured after attack by water vapor and outgassing at 300°C, but only for the adsorption on area newly created by the water. Adsorption on the original open area has been subtracted from the total amount of adsorption. Scanning behavior within the hysteresis loop is also included.

From the nitrogen isotherms obtained from the orange and grey Apollo 17 fines, outgassed at temperatures ranging from 25 to 300°C, t-plots were constructed. The reference isotherms were those measured on the same fines prior to attack by water vapor and outgassed at either 25 or 300°C. In other words, we use an internal standard in each case. The t-plot obtained for the orange fines outgassed at 300°C is reproduced in Fig. 3 together with a t-plot for the Apollo 12 (12070) which shows contrasting behavior typical of a mature soil with a long surface residence time. The t-plot for the grey fines (74241) shows an intermediate type of behavior. The plots extend to relative pressures of 1.0 and are for adsorption only on area newly developed during the attack by water vapor.

For a variety of fines, the apparent micropore areas after attack by water vapor have been determined. In Table 2 these quantities are listed as percentages of the total area created by the action of adsorbed water.

### Surface Area, Pore Volume and Pore Size Analyses

The BET specific surface areas of three different fines, Apollo 17 74220 and 74241, and the mature Apollo 16 soil 63341, before and after

exposure to water vapor are shown in Fig. 4 as a function of outgassing temperature. The areas have been normalized to the area of each sample prior to treatment with water vapor.

The pore structures of the water treated Apollo 17 fines have been analyzed using a procedure which lacks excessive refinement<sup>(18)</sup> as would befit a pore system of undoubted complexity. The cumulative mesopore volumes of the orange and grey fines, calculated from the desorption branches of the nitrogen isotherms and corrected for adsorption occurring on the original non-porous surfaces, are shown in Fig. 5. These isotherms were measured on the water vapor treated fines outgassed in the sequence of rising temperature 25, 100, 200 and 300°C. The data from the nitrogen isotherms measured prior to water sorption, also provide the reference data used to correct for the thickness of the film of nitrogen occurring on the surfaces of pores without the effects of capillary condensation.

In Table 3 the equivalent area contained within the mesopores is listed and also added to the apparent micropore area, obtained from the t-plot, and the original area of the open surface. This summed area can be compared to the BET specific surface area. The agreement is very close. If adsorption data is used to evaluate the equivalent mesopore area then the agreement is not as good. The Kelvin procedure for analyzing mesopores is carried to lower relative pressures than the closure point ( $\sim 0.5 P/P_0$ ) of the experimental hysteresis loop, in fact down to  $0.25 P/P_0$  and a Kelvin radius of about  $12 \text{ \AA}$  radius. In the area summation data of Table 3, one is taking into consideration the area of pore ranging through the whole micro and meso range of pore sizes. The maxima in the pore size distributions occur at cylinder radii of 23-25  $\text{ \AA}$ .



### Irreversibly Adsorbed Water

The weight of a sample of fines in vacuo at 25°C is known both before and immediately after the adsorption isotherm of water is measured. Assuming that there is no change in the amount of water irreversibly bound to the exterior surfaces of the grains, the change in weight is a measure of the water irreversibly adsorbed in the newly created pore system. This quantity is listed in Table 4 as  $\mu\text{g}$  of water retained after evacuation at 25°C per  $\text{m}^2$  of newly developed surface.

### DISCUSSION

There is no argument that the virgin fines are essentially non-porous to adsorbed nitrogen and that adsorbed water attacks the particles to create a fine pore system.<sup>(1)</sup> The adsorption characteristics of these pores, however, are not completely consistent with any detailed model yet advanced.<sup>(19,20)</sup>

A mechanism of fractured bridges between fused particles is proposed by Cadenhead et al.<sup>(21)</sup>, the water additionally causing swelling and a vastly increased adsorption capacity especially near S.V.P. In the case of the orange soil, the specific surface area is tripled by the exposure to water vapor near saturation vapor pressure. The reduction in the mean equivalent, spherical particle size is from 4.8 to 1.5  $\mu\text{m}$ . If adhering particles had been prised apart or fractured then changes in the particle size distribution should be readily observable in the electron microscope. The size distribution, as well as the appearance of the grains, however, is unaffected by the water vapor treatment; 80-85% of the particles are  $<2 \mu\text{m}$  in diameter with 75% of these lying in the range of size 0.1 - 0.5  $\mu\text{m}$ . The fracture hypothesis is judged by us not to be of major importance.

If the apparent changes in particle size do not affect the external dimensions of the grains, one is left to suppose that the changes are of

an internal nature. The suggested explanation<sup>(2)</sup> for the water induced pore structure in mature lunar fines is that damaged material within nuclear particle damage tracks etches preferentially. The leaching likely produces a tubular pore structure with micro-sized necks.<sup>(19)</sup>

The behavior of the Apollo 17 orange fines, and to a lesser extent the grey fines, indicates a more extensive reaction than is usual with other soils (eg 10087, 12070, 63341 and 67481 samples from Apollo 11, 12 and 16 missions respectively). There is a greater widening of channels. This interpretation is consistent with the following observations:

- (i) there is less blocking of pore volume by residual water. This effect is clearly demonstrated in Fig. 4 where for the orange fines outgassed at 25°C about 50% of the expanded area is accessible to nitrogen compared to virtually 0% in the mature fines 63341 (the blocking is nearly complete). An intermediate behavior occurs for the grey fines 74241,
- (ii) of the expanded area of the orange fines which is available to nitrogen molecules after outgassing at 300°C, 21% is apparent micropore area (calculated from the t-curve of Fig. 3). This value has varied between 35 and 70% with other fines similarly treated with water vapor. The smaller percentage in the case of fines 74220 indicates that leaching has widened the channels to the point where the micropore area is a minor fraction of the total pore area. With fewer micro-sized necks in the channel system, it is understandable that blocking by irreversibly adsorbed water is less effective,
- (iii) the quantity of irreversibly adsorbed water retained in the pore structure (Table 4) is also consistent with the smaller percentage of micropores in the orange fines. Water is, in general, retained most strongly

in the smallest channels of a pore system and requires the highest temperatures for removal<sup>(22,23)</sup>. One anticipates that where channel widening is greatest, the amount of retained water will be least. The data in Table 4 conform to this expectation with the  $\mu\text{g}$  of  $\text{H}_2\text{O}/\text{m}^2$  for the orange fines being several fold lower in magnitude than the figure obtained for the two Apollo 16 fines. The values for retained water, however, are approximate ( $\pm 10\%$ ) for the following reason. Weights of fines in vacuo are uncertain especially after conducting water vapor adsorptions within the glassware system when vacuum pressures are difficult to control closely even after overnight pumping, the minimum time of outgassing in each instance.

(iv) the t-plots seem to indicate that the pore surfaces in the Apollo 17 fines are less curved, and hence the channels are probably wider, than is the case for the usual type of regolith. It is "normal" for the t-plot to be curving upwards at  $\sim 0.5 \text{ P/P}_0$  ( $\sim 6 \text{ \AA}$  thickness), as in the case of the Apollo 12 fines 12070 (Fig. 3) where there is presumably enhanced adsorption due to capillary condensation. The effect is only very slight with the Apollo 17 fines, probably because the necessary pore curvature to promote marked capillary condensation is absent, the pores being of larger size. The downturn of the t-curves at higher relative pressures ( $> 0.7 \text{ P/P}_0$ ) can also be interpreted in the same manner. The effect, which is caused by pores filling and no longer contributing to the adsorption processes at higher relative pressures, is more pronounced with the Apollo 12 sample (12070) especially above  $t = 10 \text{ \AA}$ . This indicates the presence of smaller pores than those which exist in the Apollo

17 orange fines 74220.

Each of these behaviors viewed separately from one another may be insufficient evidence to arrive at this conclusion. Taken together, however, the case for a more developed and open pore structure for these two Apollo 17 samples from Shorley Crater is quite convincing.

Pore area, size distribution and shape

For the Apollo 17 orange and grey fines there is excellent agreement between the BET specific surface areas and the sums of the areas of the open, surface, and the areas contained within the micro and mesopores. (Table 3) Considering the uncertainties of the theories involved, as well as the experimental errors, the exceptionally close agreement in several instances must be regarded as fortuitous. One can draw several inferences, however. The pores formed by the attack of adsorbed water range continuously through the micro and meso range of sizes. There seems also to be significant differences between the pore systems formed in the grey and the orange fines. The cumulative pore volume of the grey fines, as a function of pore radius and outgassing temperature, varies in a similar manner to that found for a mature lunar soil such as the Apollo 16 sample 63341<sup>(19)</sup>. The maximum in the distribution of pore size occurs between 23-25 Å radius which is true also for the orange fines. The major difference with the orange fines lies in the larger fraction of pores a radius between 10 and 25 Å, with proportionately fewer micropores and mesopores >25 Å radius. It also seems that ridding the orange fines of irreversibly adsorbed water by increasingly severe outgassing narrows the pore size distribution for reasons unknown. The result is a hysteresis

loop whose shape, especially the adsorption branch, is intermediate between type-B and E<sup>(24)</sup>. The former type is ascribed normally to a system of open slit-shaped capillaries (or capillaries with wide bodies and short narrow necks), the latter to tubular pores with narrow open ends and constrictions or "ink-bottle" pores. The track etch hypothesis would presumably require the formation of pores having tubular shapes. The scanning behavior is, however, more like one would expect for a B-type hysteresis loop.<sup>(30)</sup>

The question arises as to why the orange Apollo 17 fines are behaving atypically with respect to pore formation. It seems paradoxical that the orange fines with so little solar wind damage and much fewer heavy nuclei damage tracks than in other mature lunar soils which we have examined, should show the most pronounced alteration after attack by adsorbed water vapor. There are, however, two clues which go part way in helping to explain the dilemma. The etching studies of Durrani et al.<sup>(10)</sup> show that in glasses irradiated with Fe ions of cosmic ray energy (232 MeV) and then etched, the diameter of the etch tracks is retarded if the glass had been irradiated also with protons of energy 3.2 MeV. Perhaps it is the virtual absence of solar wind protons in the orange fines, because they remained buried below the lunar surface, which permits the more rapid etching of cosmic ray damage tracks.

The orange Apollo 17 fines, and also the neighboring grey fines, are unique in another way which might help to explain why they are attacked by water vapor with such ease. They contain the highest fluorine (230 ppm) and chlorine (60-70 ppm) contents yet observed in lunar soils<sup>(25)</sup>, the probable source of the halogens being the fumarolic activity at the time

of their birth. Dissolution of these halogens in the sorbed water might be producing a more effective attacking agent than is generally the case when lunar fines adsorb water vapor. This possibility has been considered also by Cadenhead.<sup>(26)</sup> In fact, HF solution is normally used to obtain particle track records of lunar glass spheres by etching<sup>(10)</sup>.

The low track density ( $10^6/\text{cm}^2$ ) in the orange fines, however, still produces difficulty in explaining the large pore volume developed and the near tripling of the specific surface area. The orange fines were outgassed at  $300^\circ\text{C}$  for about 1000 minutes prior to adsorption of water vapor. This temperature and annealing time are sufficient to cause partial fading of tracks in different types of lunar glass, including the Apollo 17 orange glass<sup>(5,27)</sup>. Perhaps such an outgassing pretreatment has the effect of standardizing the residual track structure in fines where the initial track densities vary by many orders of magnitude.

To shed more light on these speculations, experiments are presently being conducted with lunar fines which have been irradiated with heavy nuclei of cosmic ray energy in the Oak Ridge Isochronous Cyclotron. The fines were first annealed at high temperatures to anneal pre-existing tracks. The results will hopefully resolve some of our difficulties of interpretation.

Actually one can deduce with a good degree of certainty that the reactivity towards water vapor is connected to the presence of damage tracks. Fines samples outgassed in vacuo at  $>700^\circ\text{C}$  lose their ability to develop porosity during water vapor adsorption<sup>(28)</sup>. These annealing

temperatures also erase the damage tracks so that they can no longer be developed by etching<sup>(5)</sup>. So it seems that the orange spherules did not possess the pore forming ability at birth since they were likely born in volcanic fire fountains from a high temperature melt. The orange spherules start melting at 1240°C<sup>(29)</sup>. The potential reactivity developed no doubt during that time period while the spherules were buried just below the lunar surface, protected from the fining action of micrometeorite impact, but being bombarded by cosmic ray nuclei. The majority of surface soils we have studied have undergone fining by micrometeorite impact, surface smoothing and cementing during exposure to solar wind, and damage when struck by heavy nuclei cosmic and solar flare particles. In these instances, it is not possible to pinpoint the source of the reactivity towards water vapor. In the case of the orange fines it is, viz the cosmic ray damage tracks.

One might be tempted to believe that the nature of the pore system and its mechanism of formation in the orange fines is markedly different than for most other lunar fines. This is because of the smaller proportion of micropores, the only slight blocking by irreversibly adsorbed water, and the different t-plot behavior. We believe this not to be the case because of the results of other studies yet to be reported<sup>(28)</sup>. If bulk liquid water rather than water vapor adsorbed close to saturation pressure is used to attack a sample of mature fines such as the Apollo 16 fines, 63341, the grains are attacked more drastically because of the much higher molar concentration of water. The resulting porosity and adsorption behavior is then nearly identical to that produced by water vapor sorption in the orange fines 74220. The differences in porosity between lunar fines seem related to differences in the degree of development of basically the same system of fine channels.

TABLE 1

Particle Sizes in the Orange Soil (74220) Before and  
After the Adsorption of Water Vapor

Particle Size Range (microns)	Frequency (%)	
	Before <u>Water Treatment</u>	After <u>Water Treatment</u>
- - - - - From 500 magnification (Figure 1A and 1B) - - - - -		
0.4 - 2	79	85
2 - 4	13	9
4 - 10	4	3
10 - 20	3	1
>20	1	2
- - - - - From 10,000 magnification (Figure 1C and 1D) - - - - -		
0.02 - 0.1	13	11
0.1 - 0.2	30	28
0.2 - 0.5	42	43
0.5 - 1.0	15	18



TABLE 2

Apparent Micropore Area as a Percentage  
of the Total Area\* within Pores

<u>Apollo 17</u>		<u>Apollo 12</u>	<u>Apollo 16</u>		<u>Apollo 14</u>
orange 74220	grey 74241	12070	63341	67481	14003
21%	42%	35%	35%	37%	69%

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\*Data obtained from isotherms of nitrogen after outgassing the fines  
at 300°C.

TABLE 3

Areas of Open Surface and Apparent  
Areas Contained Within Micro and  
Mesopores in Apollo 17 Fines

a. Orange Fines 74220

	Outgassing temperature (°C)			
	25	100	200	300
S open	0.36	0.36	0.42	0.42
S micro	0.17	0.19	0.26	0.20
S meso	0.43	0.46	0.68	0.72
S open + S micro + S meso	0.96	1.01	1.36	1.34
S BET	0.91	1.02	1.40	1.38

b. Grey Fines 74241

	Outgassing temperature (°C)			
	25	100	200	300
S open	0.36	0.36	0.37	0.37
S micro	0.16	0.20	0.18	0.27
S meso	0.19	0.21	0.32	0.37
S open + S micro S meso	0.71	0.77	0.87	1.01
S BET	0.57	0.65	0.88	1.01

All S values are in  $\text{m}^2 \text{g}^{-1}$ , S meso values are obtained from the desorption branches of the nitrogen isotherms above a relative pressure of 0.25, S micro values are obtained from t-plots.

TABLE 4

Water Irreversibly Adsorbed at 25°C Per  
Square Meter of Newly Developed Area

Sample	Water Retained in Pores ( $\mu\text{g H}_2\text{O}/\text{m}^2$ )
Apollo 17 Orange Fines 74220	250
Apollo 17 Grey Fines 74241	700
Apollo 16 Fines 63341	1000
Apollo 16 Fines 67481 (North Ray Crater)	1700

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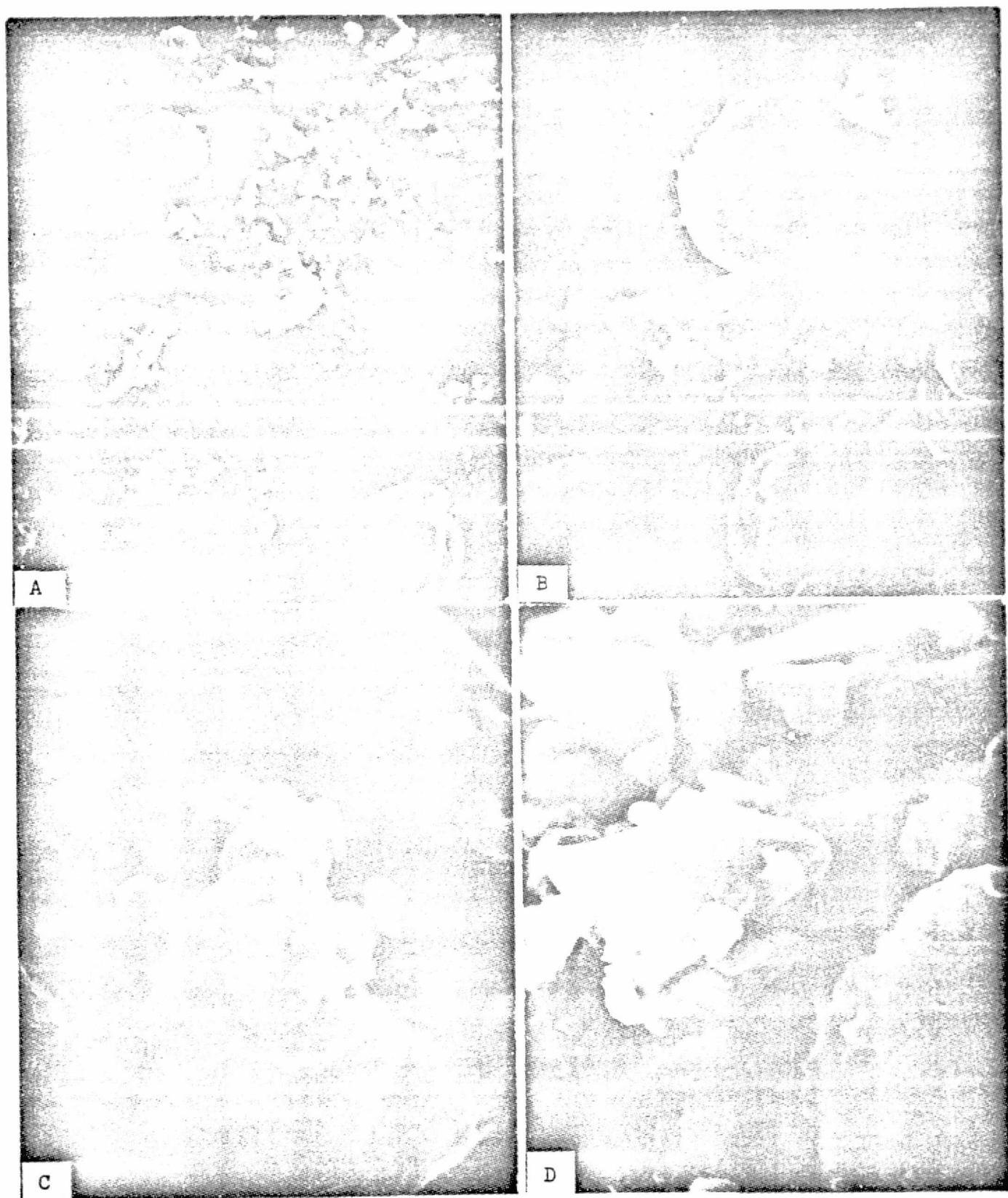


Fig. 1. Scanning electron micrographs of the orange soil (74220).  
A. Before water treatment (500X). B. After water treatment (500X).  
C. Before water treatment (10,000X). D. After water treatment (10,000X).

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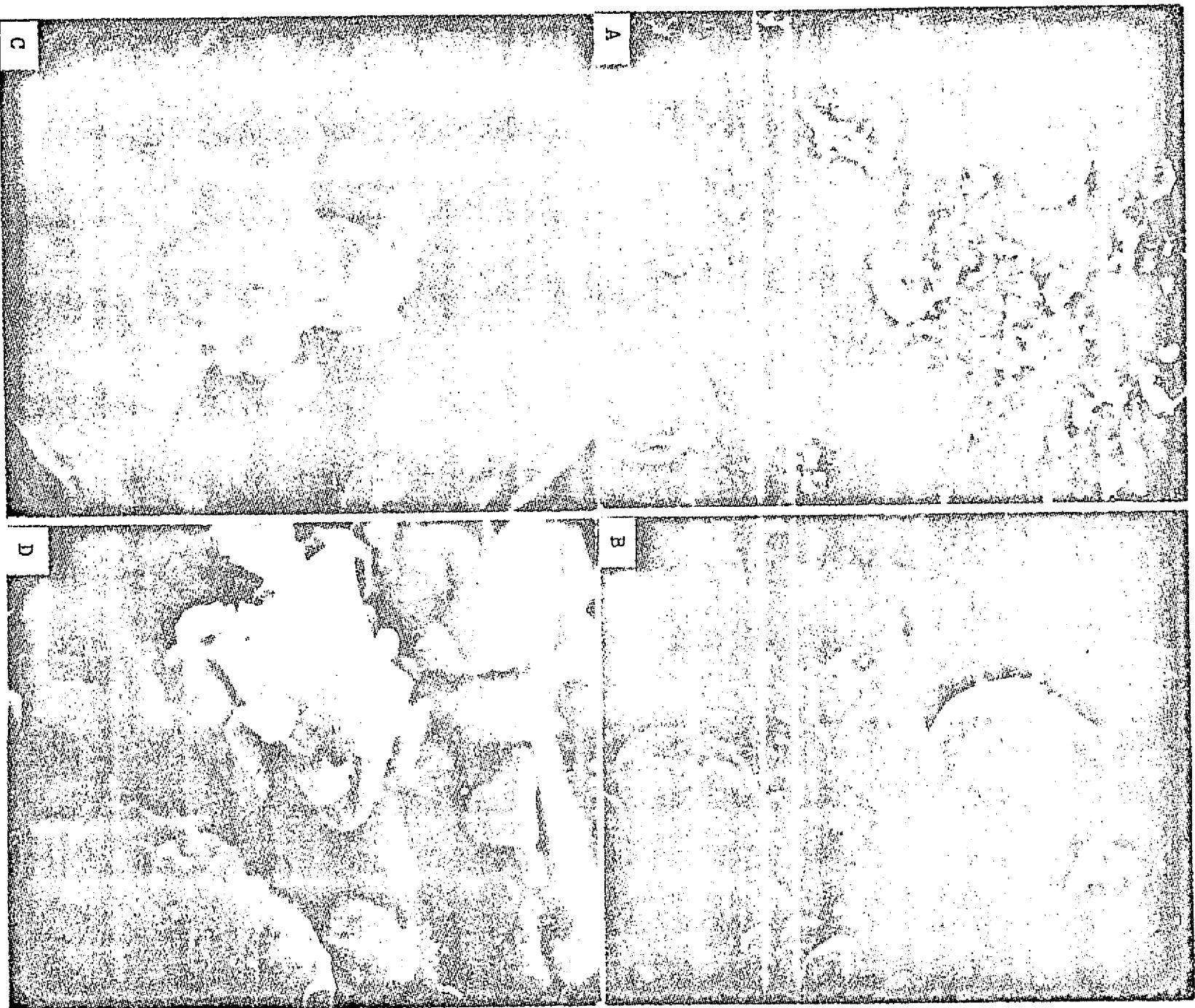


Fig. 1. Scanning electron micrographs of the orange soil (74220).  
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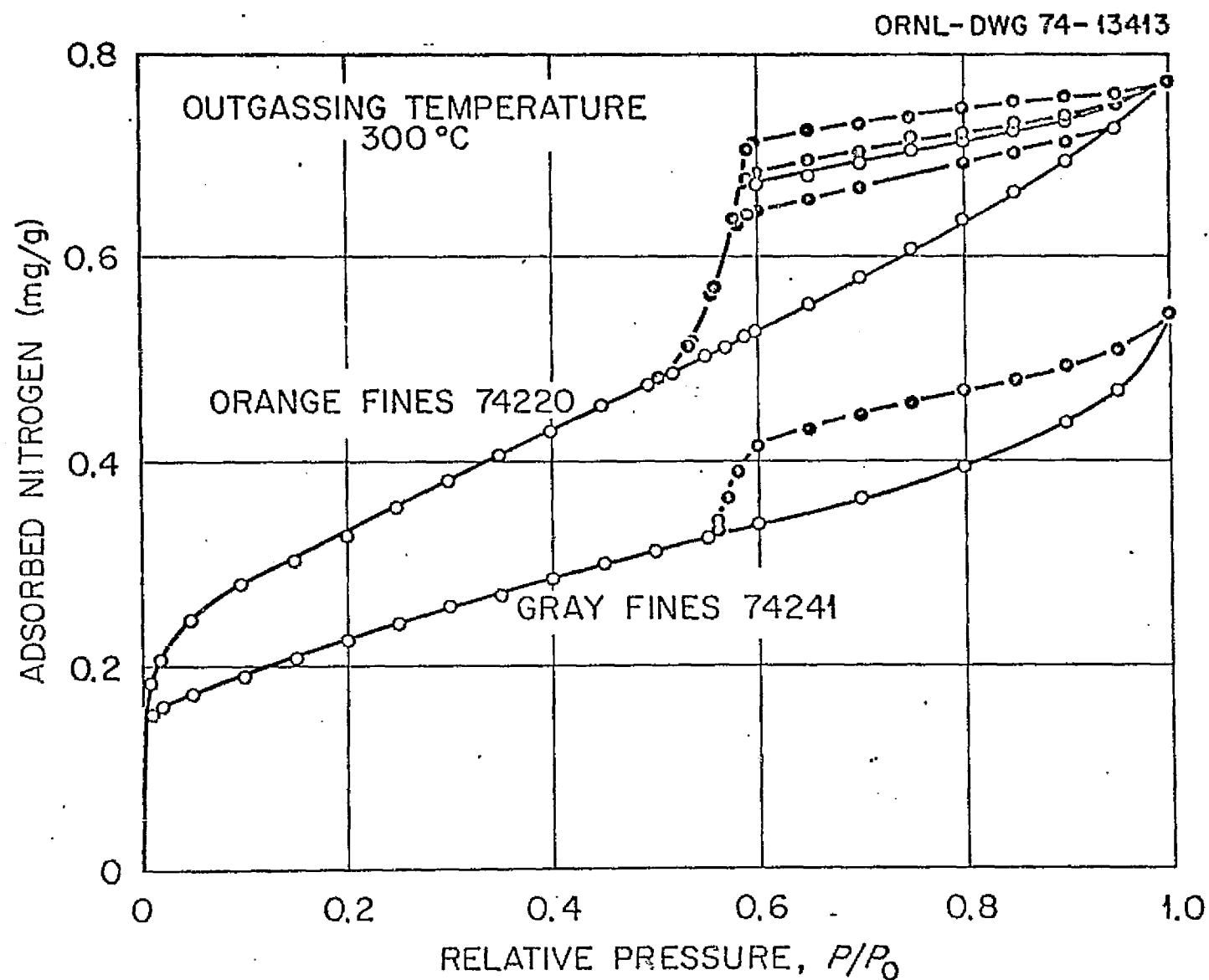


Fig. 2. Adsorptions of nitrogen on the newly developed areas of Apollo 17 fines; o adsorption, • desorption.

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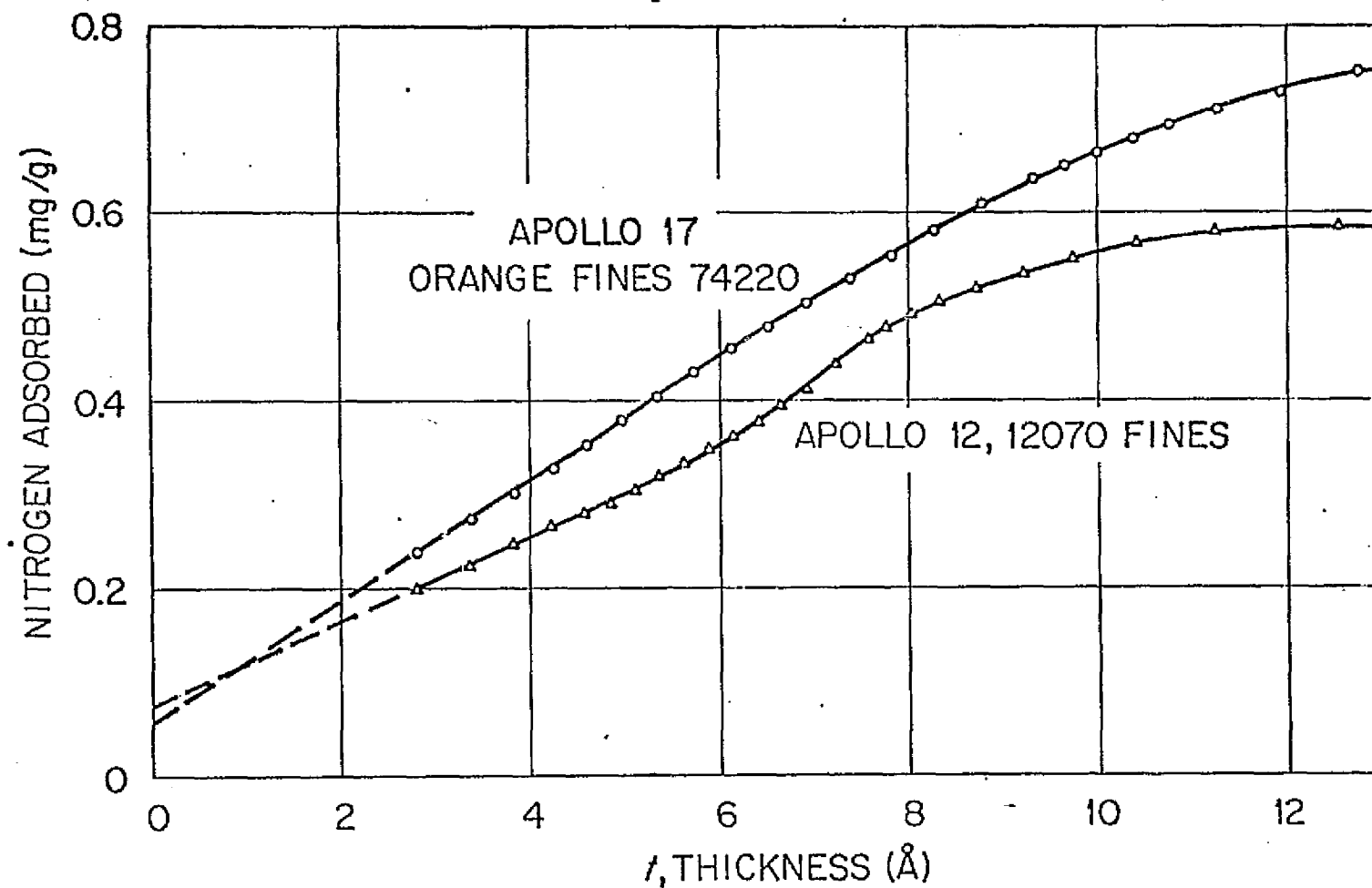


Fig. 3. t-plots of adsorbed nitrogen on fines reacted with water vapor and then outgassed at 300°C.

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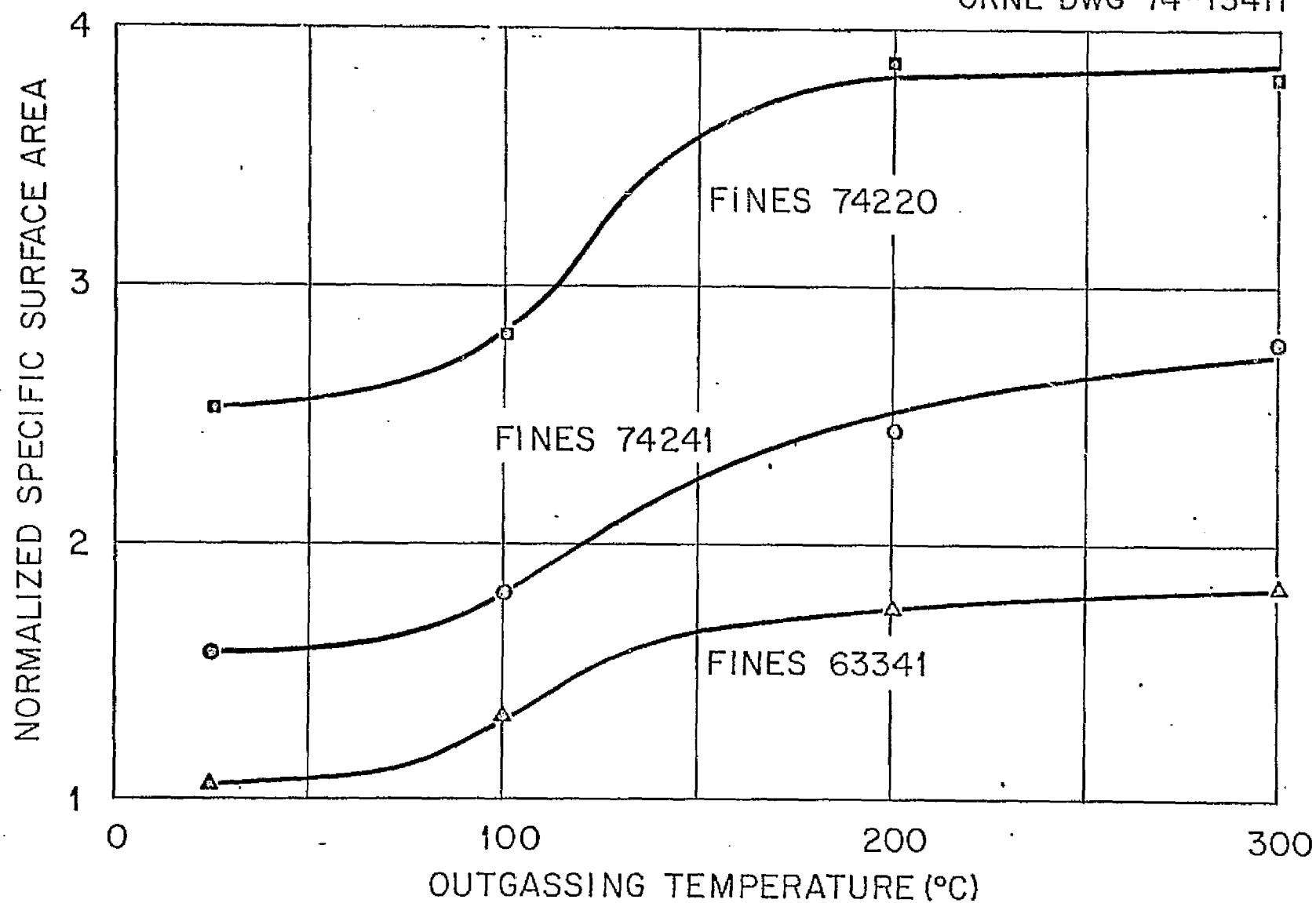


Fig. 4. Variation in specific surface area of fines reacted with water vapor as a function of outgassing temperature; normalizations are to the area of each sample prior to adsorption of water vapor.

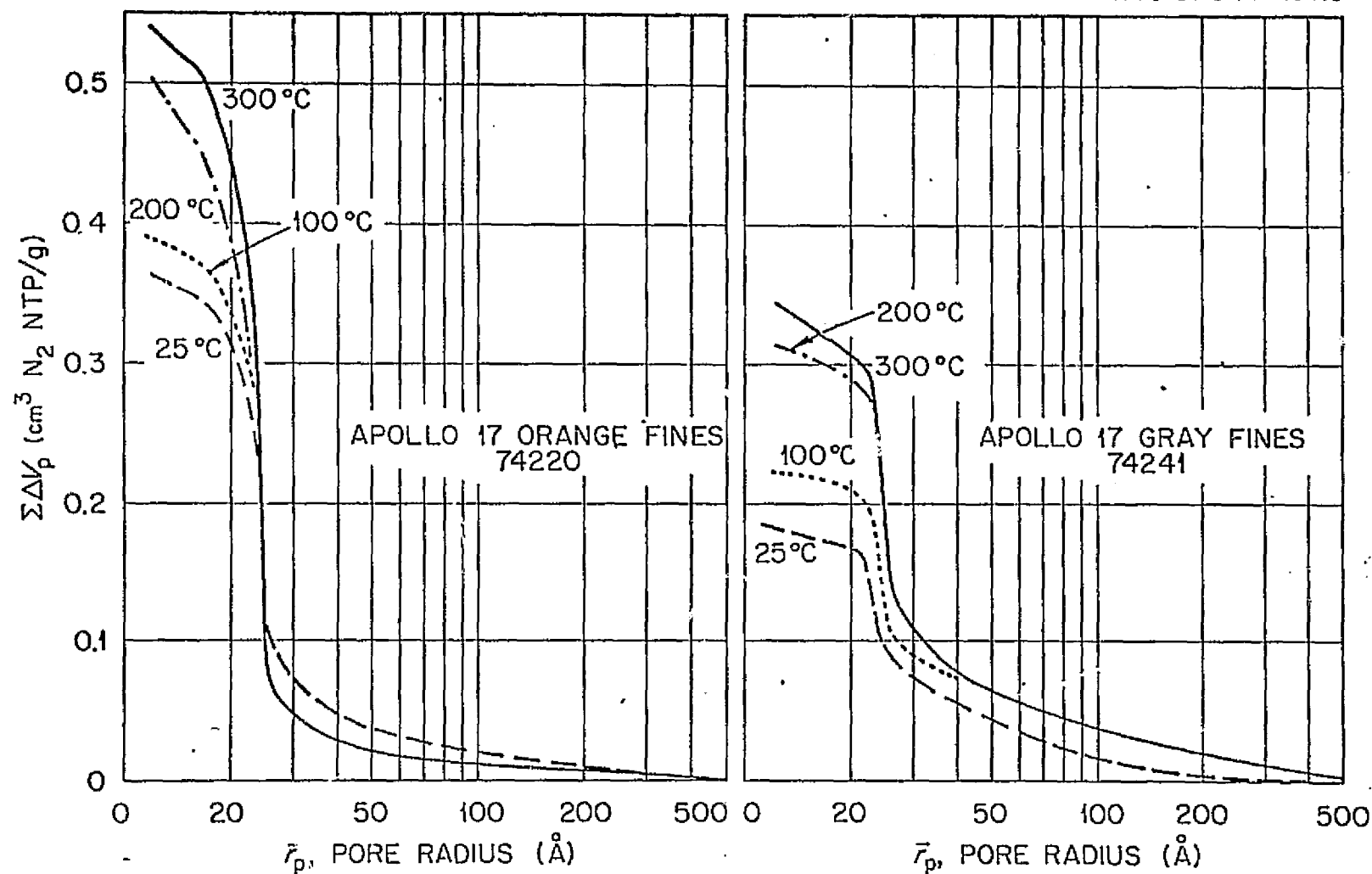


Fig. 5. Cumulative pore volumes calculated from the desorption branches of nitrogen isotherms measured after outgassing the water vapor treated fines at 25, 100, 200 and 300°C.

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INTERACTION OF GASES WITH LUNAR MATERIALS: REVISED

RESULTS FOR APOLLO 11\*

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\*Research carried out under Union Carbide's contract with the  
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## ABSTRACT

The surface properties of an Apollo 11 soil sample have been reinvestigated. The present study shows that the preliminary results for this sample (Fuller et al., 1971) are in error, principally because of incorrectly applied instrumental background effects. The surface properties of these Apollo 11 fines are very similar to those of fines from the other Apollo landing sites that we have examined. On the basis of results reported to date, the surface properties of lunar soil samples are, to a first approximation, independent of chemical composition and location on the lunar surface. Drastic alteration of the surface characteristics of lunar fines by adsorbed water continues to be the distinguishing feature of their surface chemistry.

## INTRODUCTION

Lunar fines from the Apollo 12, 14, 16, and 17 missions, although differing in certain specific aspects, have certain uniform surface characteristics (Holmes et al., 1973a; Holmes et al., 1974). These later studies gave markedly different results from those obtained in an earlier preliminary study of an Apollo 11 sample (Fuller et al., 1971). The preliminary study indicated that lunar fines have remarkably low surface energies, resulting in linear (to saturation pressure) isotherms for the adsorption of argon and oxygen. Subsequent results with other samples showed that the physical adsorption of gases such as nitrogen and argon on lunar fines was not unusual. Water isotherms obtained in the preliminary study were also abnormal, having vertical steps in the adsorption and desorption branches at relative pressures of 0.9 and 0.8, respectively. The early studies also indicated that the interaction with water had no effect on the subsequent physical adsorption of gases. This is in distinct contrast to later studies (e.g., Holmes et al., 1974) in which all samples examined could be drastically altered by a strong interaction with adsorbed water at pressures approaching saturation. The alteration consisted of a marked increase in specific surface area (by as much as a factor of three) and the creation of pores. In view of these discrepancies, it seemed desirable to reexamine the surface properties of the same Apollo 11 lunar fines to determine the authenticity of the preliminary results.

# EXPERIMENTAL

Adsorption measurements were made with an existing vacuum microbalance system which has been described in detail (Fuller et al., 1965). The system has been equipped with a device for maintaining a constant pressure of water vapor during equilibration at each chosen pressure (Fuller et al., 1972). Background blank corrections have been applied to all of the data. These corrections, and their critical importance for accurate acquisition of adsorption data for samples having small specific surface areas, have been discussed (Cadenhead et al., 1972; Holmes et al., 1973b).

Experimental procedures were generally the same as before (e.g., Holmes et al., 1973a). Prior to an adsorption experiment the sample was always outgassed (at a pressure of  $10^{-5}$  to  $10^{-6}$  torr) at the chosen temperature for a minimum of 16 hours (overnight). Measurement of the isotherms required 15 to 20 minutes for equilibration at each pressure except for water vapor which, at high relative pressures, required an overnight waiting period, or longer, for equilibration with the fines. Weight determinations are estimated to be reliable to  $\pm 2$  micrograms ( $\pm 0.005$  mg/g) over the extended time interval involved in the experiments.

The specific sample used in the present study was a 400 mg aliquot of lunar fines sample 10084,66 from the Apollo 11 mission. This sample was the fine sieve fraction ( $< 1$  mm) of lunar soil and was used without further size classification. Major element composition of this sample (expressed as the oxide) was  $\text{SiO}_2$  (41.78%),  $\text{FeO}$  (15.65%),  $\text{Al}_2\text{O}_3$  (13.47%),  $\text{CaO}$  (12.13%),  $\text{MgO}$  (8.07%), and  $\text{TiO}_2$  (7.41%). Other elemental oxides were present at less than one percent by weight. Major mineral phases present were anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ , 34.65%), hypersthene  $[(\text{Mg}, \text{Fe})\text{SiO}_3]$ , 23.18%, diopside ( $\text{CaMgSi}_2\text{O}_6$ ,



20.42%), and illmenite ( $\text{FeTiO}_3$ , 14.07%). Other phases were present in much smaller amounts. (These results are taken from LSPET, 1973b.)

The specific sample used in the preliminary measurements (Fuller et al., 1971) was 10087,5. The only difference between 10087 and 10084 was in their initial processing at the Lunar Receiving Laboratory. Sample 10037 was processed inside a vacuum chamber while sample 10084 was processed in the normal manner (in a dry nitrogen atmosphere) (Annexstad, 1974). However, both samples were exposed to air for several months prior to loading on the vacuum microbalance. Therefore, it is our contention that these two samples should have had identical surface properties at the start of the adsorption experiments.

#### RESULTS AND DISCUSSION

Adsorption isotherms of the physically adsorbed gases nitrogen, argon, carbon monoxide, and oxygen at 77°K (-196°C) are shown in Figure 1. Prior to these measurements the sample was outgassed at 300°C, the same pretreatment used in the preliminary study. These present measurements (Figure 1) can be contrasted with Figure 1 of the preliminary results (Fuller et al., 1971). The adsorption isotherms shown in Figure 1 are not unusual and are also very similar to our results (Holmes et al., 1973a; Holmes et al., 1974) obtained for all other samples we have studied except 10087. Adsorption data for these four gases were subjected to a BET treatment (Brunauer et al., 1938) to obtain an estimate of the specific surface area. The values are given in Table I along with the corresponding areas from the preliminary results for sample 10087 (Fuller et al., 1971). An average of the four

areas for 10084 is  $0.50 \pm 0.05 \text{ m}^2/\text{g}$ . This lies within the range of areas ( $0.2$  to  $0.6 \text{ m}^2/\text{g}$ ) reported for a host of different lunar fines (e.g., Cadenhead et al., 1974; Fanale et al., 1971; Grossman et al., 1972; Holmes et al., 1973a) but is considerably less than the preliminary value of  $1.15 \text{ m}^2/\text{g}$  for 10087. Also given in Table I are the cross-sectional areas,  $A_m$ , used in the specific surface area calculations. The  $A_m$  values used for argon are significantly different while the same  $A_m$  value was used for nitrogen in both cases. The choice of the best  $A_m$  value for various gases is outside the scope of the present paper but has been discussed (McClellan and Harnberger, 1967).

Following an additional outgassing at  $300^\circ\text{C}$ , sample 10084 was subjected to an adsorption-desorption cycle in water vapor at  $20^\circ\text{C}$ . [The first experiment in water vapor was affected by a small leak in the vacuum system. The significance of this small leak is discussed in a companion paper (Gammage and Holmes, 1975). The second experiment was successful after the leak was repaired.] Adsorption data from the first experiment are shown in Figure 2. (Relative pressures have been corrected to account for the leak. Unfortunately, in order to conserve time, equilibrium data were not taken during the second experiment. However, there were no indications of abrupt weight increases or decreases as the water vapor pressure was slowly increased or decreased, respectively.) The present isotherm can be contrasted with Figure 2 of the preliminary results obtained with sample 10087 (Fuller et al., 1971). Conspicuously absent in the isotherm for 10084 are the sharp vertical steps at relative pressures of  $0.9$  and  $0.8$  in the adsorption and desorption data, respectively. The present data are quite similar to that observed for lunar

finer than 10087, e.g., 12001 and 63341 (Holmes et al., 1973a). In agreement with the usual behavior of lunar fines, there was extensive retention of water (0.39 mg/g in this case) on evacuation at the conclusion of the adsorption-desorption cycle.

The preliminary results (Fuller et al., 1971) indicated that the interaction with water vapor did not produce any significant change in the adsorptive capacity for nitrogen. This is in direct contrast to our results with all succeeding samples which have interacted strongly with water (e.g., Holmes et al., 1974). Nitrogen adsorption (at 77°K) on sample 10084 was also measured after the reactions with water vapor. Isotherms for two outgassing temperatures (22 and 300°C) are shown in Figure 3. It is obvious that the sample has been significantly altered by the reaction with water vapor. In particular, the specific surface area has increased to 0.94 and 1.24 m<sup>2</sup>/g for room temperature (22°C) and 300°C outgassing, respectively. In addition, the sample now has a pore system which gives rise to a well-defined capillary condensation hysteresis loop in the adsorption-desorption isotherm. Furthermore, irreversibly adsorbed water remaining on the sample after outgassing at room temperature has a partial blocking effect on the access of nitrogen to the pore system. All of these results are in agreement with the general surface characteristics of other lunar fines.

We are forced to conclude that the preliminary results (Fuller et al., 1971) obtained with sample 10087 are erroneous. The erroneous isotherms for the inert gases on sample 10087 can be readily attributed to our failure to apply accurate blank corrections (Holmes et al., 1973b; Cadenhead et al., 1972). An additional complication was the fact that only 100 mg of 10087

was available for study. However, the erroneous water isotherms for sample 10087 and the unchanged surface properties after reaction with water remain unexplained.

In a general way, the surface properties of Apollo 11 fines seem to be quite similar to those of fines from the Apollo 12, 14, 16, and 17 missions (Holmes et al., 1973a; Holmes et al., 1974). [We have not studied any fines from the Apollo 15 mission. Cadenhead (Cadenhead et al., 1974) obtained a hysteresis loop in the initial nitrogen isotherm for an Apollo 15 sample, but it was a breccia, not a soil sample. Grossman et al. (1972) measured the surface area of an Apollo 15 sample but did not report an isotherm.] It is pleasing and, at the same time, somewhat puzzling that the surface properties of soil samples from five of the six successful Apollo missions are so uniformly general. [Results from a compacted soil from Apollo 15 (Cadenhead and Stetter, 1974) do not give any indication that Apollo 15 soils are different.] There are certain specific differences in the surface properties of lunar samples, most notably in the relative ease with which an adsorbed water film alters their surface characteristics, but these subtle differences are beyond the scope of the present paper. The general uniformity of the surface properties of lunar soil samples does not seem to be related to bulk composition as there is substantial variation in the chemical composition of the samples. For example, the orange soil 74220 has only 6.32%  $\text{Al}_2\text{O}_3$  (LSPET, 1973b) while the Apollo 16 sample 67481, having similar surface properties (Holmes and Gammage, 1975), has 29.01%  $\text{Al}_2\text{O}_3$  (LSPET, 1973a). The mineralogy and petrology of the samples show a larger variation than the chemical composition. We hold to our earlier interpretation (Holmes et al., 1973a) that radiation damage is the prime factor involved in the alteration

of lunar fines samples by adsorbed water. Results from experiments with a thermally annealed and artificially irradiated sample (Holmes et al., 1975) provide support for this conclusion.

#### ACKNOWLEDGEMENTS

The authors would like to thank Prof. P. H. Emmett for several stimulating discussions. This research was sponsored by NASA under Union Carbide contract with the U.S. Energy Research and Development Administration.

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Table I. Data for Adsorption of Inert Gases

Adsorbate	Sample 10037			Sample 10084		
	$S^a$	$C^b$	$Am^c$	$S^a$	$C^b$	$Am^c$
$N_2$	1.1 <sub>5</sub>	14	16.2	0.59	45	16.2
Ar	1.1 <sub>4</sub> <sup>d</sup>	--	13.8	0.46	20	16.6
CO	1.1 <sub>5</sub>	130	16.2	0.50	62	16.8
$O_2$	e	--	--	0.46	23	17.5

<sup>a</sup>Specific surface area in  $m^2/g$ .

<sup>b</sup>"C" constant in BET equation (Brunauer et al., 1938).

<sup>c</sup>Cross-sectional area of an adsorbed molecule in  $\text{\AA}^2$ .

<sup>d</sup>Assumes monolayer coverage at saturation pressure.

<sup>e</sup>Not calculated.

## List of Figures

Figure 1. Adsorption of inert gases on sample 10084,66 at  $-196^{\circ}\text{C}$ .

Sample outgassed at  $300^{\circ}\text{C}$ .

Figure 2. Adsorption of water on sample 10084,66 at  $20^{\circ}\text{C}$ . Sample

outgassed at  $300^{\circ}\text{C}$ .

Figure 3. Adsorption of nitrogen on sample 10084,66 at  $-196^{\circ}\text{C}$  after the interaction with water. Sample outgassed at indicated temperatures.

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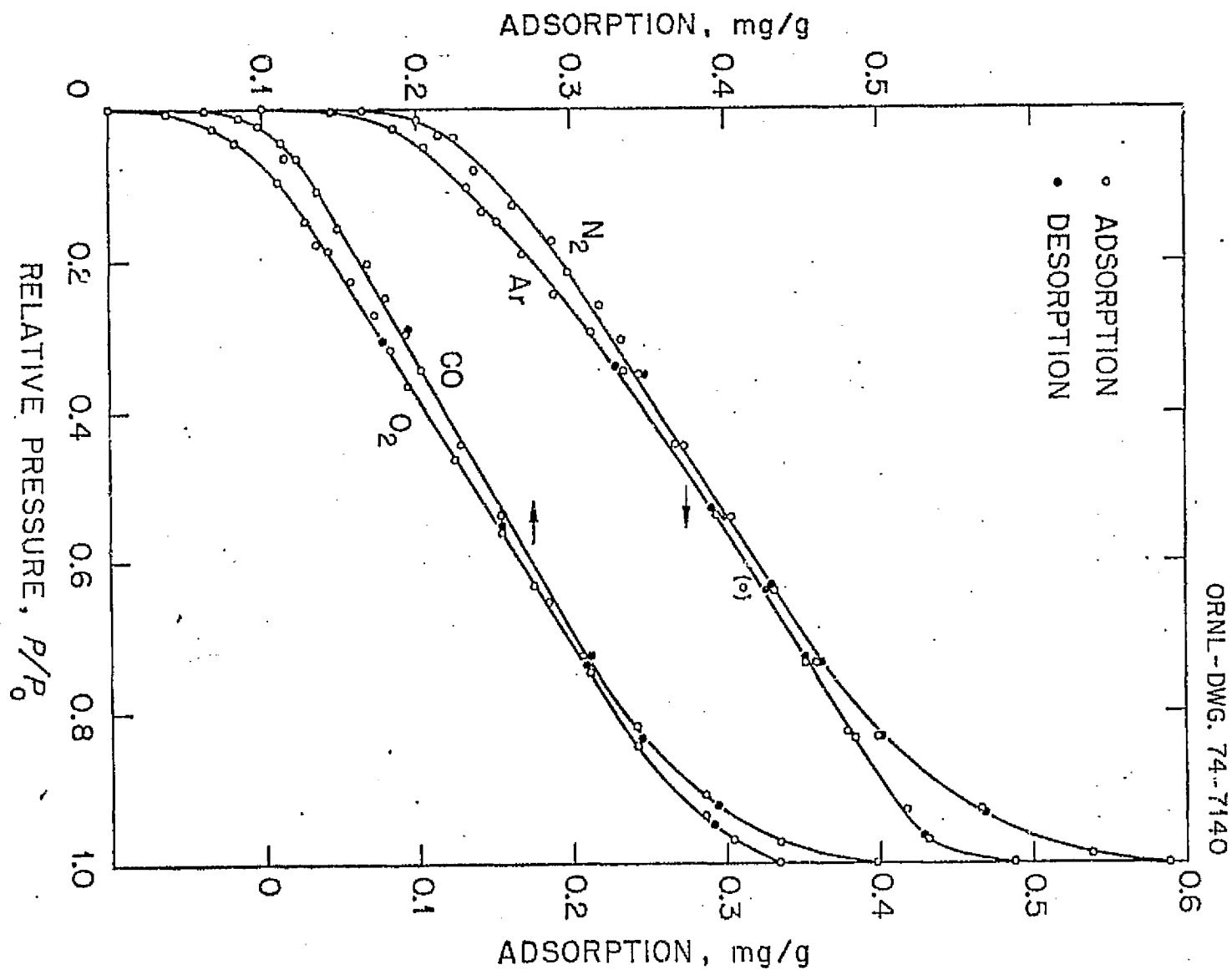


Figure 1. Adsorption of inert gases on sample 10084,66 at  $-196^\circ\text{C}$ . Sample outgassed at  $300^\circ\text{C}$ .

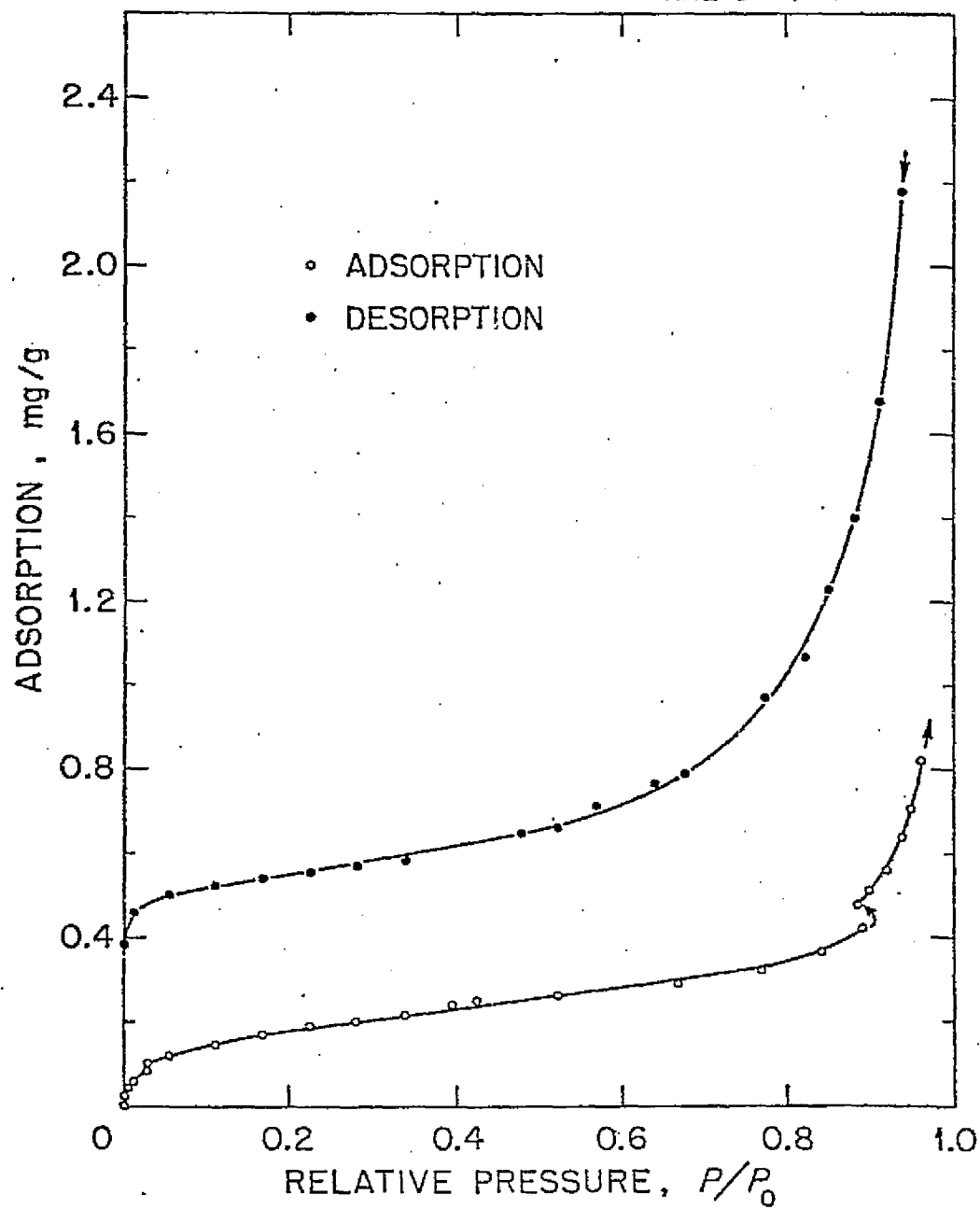


Figure 2. Adsorption of water on sample 10084,66 at 20°C. Sample outgassed at 300°C.

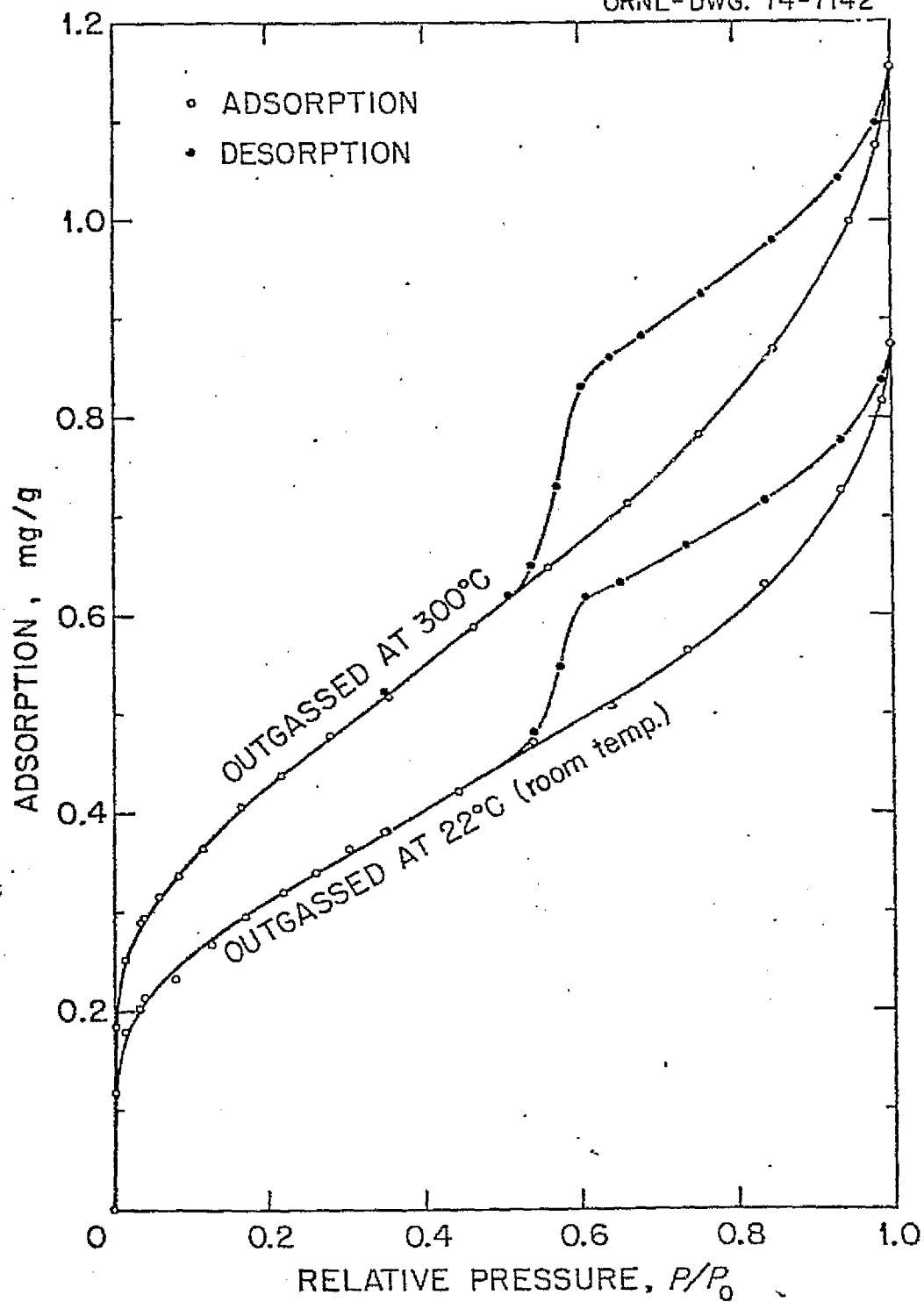


Figure 3. Adsorption of nitrogen on sample 10084,66 at  $-196^{\circ}\text{C}$  after the interaction with water. Sample outgassed at indicated temperatures.

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BLOCKING OF THE WATER-LUNAR FINES REACTION  
BY AIR AND WATER CONCENTRATION EFFECTS\*

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ABSTRACT

The elements of air, if adsorbed in conjunction with water vapor or liquid water, are able to impede severely the attack of lunar fines. Thus is explained the stability of lunar fines in moisture laden air, and their small solubility in liquid, aerated water. In the absence of air, liquid water is more effective than water vapor in attacking the grains; the channels leached are wider and the expansion of area is greater.

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## INTRODUCTION

Grains of dust on the lunar surface are irradiated with solar wind particles having an average ion energy of 1 keV/amu. (Maurette and Price, 1975). The helium and hydrogen ions cause the grains to become severely rounded by ion sputtering and coated with sputtered material, processes which leave the grains non-porous on a size scale from about 5 to 500 Å (Gammage et al., 1974a). An ultrathin, amorphous surface layer is formed by the overlap of the ~100 Å length tracks produced predominantly by helium ions (Borg et al., 1971).

The sputtering by He ions builds up an equilibrium coating thickness, which takes ~2000 years for lunar feldspar grains (Maurette and Price, 1975). The coating propagates with constant thickness into a shrinking grain as sputtering removes the outer atoms. The erosion rate varies greatly with the type of mineral; glassy grains erode the fastest.

Submicron grains are unlikely to survive collisions with micrometeorites which tend to fine the larger dust particles. Mature surface soils subjected to these processes tend towards a limiting specific surface area of about  $0.6 \text{ m}^2/\text{g}$ , the equivalent spherical particle being about 3.4 μm. The specific surface area is a maturity index of a lunar soil (Gammage and Holmes, 1975a).

Surface grains also become riddled with damage tracks from heavy ions ( $Z > 20$ ) having energies  $> 5 \text{ keV/amu}$ . These are ions with suprathermal energies, solar flare particles and cosmic rays. The tracks range in length from  $< 2$  to several hundred μm. Track densities as high as  $10^{11} \text{ cm}^{-2}$  can be seen in the transmission electron microscope.

It is on such damaged grains that adsorbed water can produce drastic alterations (Holmes et al., 1973a; Holmes et al., 1973b), that is to expand the surface area by as much as threefold, and at the same time develop porosity. The currently described experiments seek to define the conditions under which water will or will not attack the grains at damage sites, how changes in the concentration of water influence the reaction, and to throw more light on the types of pore structure that develop.

This knowledge is of considerable practical importance. One is interested in knowing how stable the fines are in the presence of atmospheric moisture, their solubility in liquid water and the details that are revealed of the fine structure of the damage tracks.

#### EXPERIMENTAL

The vacuum microbalance systems and the procedures required to make accurate measurements of gases adsorbed on lunar fines have been dealt with numerous times in the past (e.g. Holmes et al., 1974). The major difference to the study presently being reported lies in the manner of reacting the lunar fines with water. Previously, the lunar fines have been outgassed in vacuo, in the range of temperature 25-300°C, and then exposed to water vapor up to SVP (Saturation Vapor Pressure). Three additional treatments have been added. Firstly, air was leaked into the vacuum system such that the maximum pressure exceeded the SVP of water by 1 torr. This introduction of air actually occurred inadvertently via a leaking stopcock. The second procedure involved cooling the fines in the sample bucket on the microbalance to liquid nitrogen temperature, and then condensing water vapor onto the fines which had been evacuated at 300°C to  $10^{-5}$ - $10^{-6}$  torr prior to this condensed



water treatment. The third treatment was to soak the fines in distilled water, exposed to the atmosphere, for 30 days. Preliminary drying was effected by evaporation of all the liquid in the presence of a desiccant. Final drying was conducted after loading the fines onto the microbalance and pumping out the system to a high vacuum ( $<10^{-5}$  torr).

Two specimens of mature lunar regolith (heavily radiation damaged) were used; Apollo 11, fines 10084 and Apollo 16, fines 63341.

## RESULTS

The specific surface areas determined from adsorptions of nitrogen as a function of the type of water treatment, and the outgassing temperature, are shown in Fig. 1. The areas are each normalized to the value obtained prior to treatment with water, and for an outgassing temperature of 25°C. The one exception is an aliquot of the fines 63341 which was soaked in water before a measurement was ever made of its specific surface area which was then  $0.51 \text{ m}^2/\text{g}$ . The non-water treated aliquot of the fines 63341 had a lesser area of  $0.42 \text{ m}^2/\text{g}$ . The difference in area could be due to inhomogeneities in our sampling of 400 mg aliquots of dust which contain grains up to 1 mm in diameter. The dotted pathways are those estimated from a comparison with more complete data collected for the Apollo 17 orange fines 74220, which were also severely attacked by water (Gammage and Holmes, 1975b).

The specific surface areas of the single aliquot of the fines 10084 are tabulated (Table 1) to highlight the very weak and the strong alterations produced by water vapor-air and air free, condensed water vapor, respectively. On this single aliquot, the water vapor treatment preceded the condensed water treatment. The differing degrees to which aerated liquid water,

water vapor at close to SVP, or air free, condensed water vapor have altered the fines 63341, are characterized by the three nitrogen isotherms shown in Fig. 2; the outgassing temperature is standardized at 300°C. The isotherms of nitrogen shown in Fig. 3 highlight the different characters of the isotherms which result after the milder (water vapor at SVP) and the most severe (condensed water vapor) water treatments and outgassing at only 25°C. To judge the relative accessibilities of nitrogen to the water induced pore system as a function of outgassing temperature, A and B of Fig. 3 should be compared to B and C, respectively, of Fig. 2. A similar estimation of accessibility of nitrogen to the pore system of the severely attacked fines 10084 can be made by viewing the two isotherms of Fig. 4; analysis of the desorption branches of the isotherms above a  $P/P_0$  of 0.25 (Gammage et al., 1974b) indicates that about 75% of the pore volume, capable of being reached by nitrogen molecules at 77°K, is reached after outgassing at 25°C. The corresponding value for fines attacked more mildly by water vapor is about 50% (Gammage et al., 1974b).

The Taurus Littrow orange soil 74220, of the Apollo 17 mission, has been outgassed at 300°C and subjected to adsorptions of water vapor by two different groups, ourselves (Holmes et al., 1974) and Cadenhead's group (Cadenhead and Stetter, 1974); Fig. 5 compares the desorption isotherms of water measured at room temperature and Fig. 6, the subsequently measured isotherms of nitrogen on the well outgassed fines (150° or 300°C). The nitrogen specific surface areas before and after the adsorptions of water vapor are listed in Table 2.

The amount of adsorbed water which becomes irreversibly bound to the newly created area of a fines sample (that water which cannot be removed by prolonged pumping at 25°C for 16 hours to a pressure of  $10^{-5}$ - $10^{-6}$  torr) is influenced markedly by the severity of the water treatment. Typical values are listed in Table 3.

In view of the observation that in the presence of air, the attack of fines by water is severely impeded, attempts were made to measure the adsorptions of nitrogen, oxygen and carbon dioxide at room temperature. No adsorption ( $<2 \mu\text{g}$ ) could be detected for any of these gases before or after the interaction of fines with water.

#### DISCUSSION

When lunar fines are brought into contact with water contaminated by air, the normally drastic alterations to the fines (Holmes et al., 1973a; Holmes et al., 1973b) are prevented almost entirely. The data in Table 1 for the fines 10084 clearly illustrate the effect; when the water vapor is contaminated by 1 torr of leaked air, the area expansion is unable to occur. A similar effect is obtained for liquid water with dissolved air; curve B of Fig. 1.

This finding suggests a satisfactory solution to the several dilemmas created by the experiments of other workers which have suggested a considerable stability for lunar fines stored in contact with moisture containing laboratory atmospheres at room temperature (e.g. Gammage and Becker, 1971). The explanation also seems to be at hand for the lower solubility of Apollo 12 fines 12070 compared to terrestrial basalt (Keller and Huang, 1971); presumably the water used contained dissolved air. The lunar fines will be attacked only when pains are taken to exclude rigorously the elements of air from either the water vapor or liquid water.

As to the nature of the blocking action, one can do little but speculate at this stage of experimentation. Each of the reactive constituents of the atmosphere ( $O_2$  and  $CO_2$ ), together with nitrogen, are not adsorbed on the fines to the extent that the adsorption is detected by the microbalance. If these molecules are chemisorbed at points where nuclear particle damage tracks intersect the surface (the proposed sites for initiation of the alteration reaction by adsorbed water) then for dust grains with  $10^{11}$  tracks  $cm^{-2}$ , 0.28, 0.32 and 0.44  $\mu g$  of  $N_2$ ,  $O_2$ , and  $CO_2$ , respectively, would be taken up. These values are for a 1 g sample having a surface area of  $1 m^2$  with the assumption that 1 molecule is chemisorbed per damage track to promote the blocking action. The amount of chemisorption would need to be 5  $\mu g$  or more to make a positive identification since adsorptions are likely to be in error by  $\pm 2 \mu g$  (Holmes et al., 1974) for the 400 mg aliquot of each fines sample used.

In order to determine whether or not each of these separate constituents of air can exert the blocking effect, they would have to be added in turn to water vapor being admitted to well outgassed lunar fines. Our future plans do not include such experiments.

Oxygen is known, however, to chemisorb on freshly produced lunar rock surfaces at the sites of ruptured bonds (Haneman and Miller, 1971). The amount taken up is small, 1 in  $10^4$  surface atoms is involved, but the oxygen desorbs from the paramagnetic sites under high vacuum. Perhaps oxygen can likewise be chemisorbed at damage sites and prevent the ingress of water.

The issue of air contaminant and the water reaction is likely to be the cause of the divergent results, obtained by separate groups of investigators, from the same sample of fines. The specific surface areas quoted in Table 2, and the isotherms of Figs. 5 and 6, make it irresistably tempting to suggest that Cadenhead's specimen of the orange fines 74220 was not severely attacked because of a contamination problem of some sort.

The molar concentration of liquid water at 25°C is 3600 times that of water vapor at SVP; liquid water is thus able to attack the fines more aggressively than the vapor. The result is a greater expansion in the surface area as evidenced, for example, by the nitrogen isotherms shown in Fig. 2.

Another difference is that the pore channels, which produce capillary condensation and the hysteresis loops in the nitrogen isotherms, are wider when liquid water is the medium. Traces of water left behind after subsequence evacuation are less able to hinder the entry of nitrogen molecules at 77°K. This effect is illustrated clearly in a comparison of the curves A and C of Fig. 1 and the isotherms of Figs. 3 and 4.

The data suggest the following interpretation. Water acts as a mild etching agent. Material is leached from nuclear particle damage tracks which remain after outgassing at 300°C. Some recent studies of irradiated mica (Maurette and Price, 1975) provide a clue as to the likely dimensions of the damaged regions; small clusters of defects form along the paths of the incident ions and these coagulate into larger clusters that reach a maximum size of 20 Å as the annealing temperature is raised to 300°C.

The adsorptions of nitrogen measured on lunar fines treated with water vapor are indicative of a system of small channels with narrow micro-sized necks up to about 20 Å in width (Everett, 1972 for definitions of micro and mesopores). Water not removed by outgassing at room temperature is held in the micro-sized constrictions and partially blocks the access of subsequently adsorbed nitrogen molecules. Cooperative adsorption forces acting across a micropore bond residual water more effectively than is the case for the wider mesopores (20-500 Å in width) which are prevalent after the use of air free, liquid water.

The different capacities for retaining water in vacuo are quantified in Table 3, and Table 4 of the reference of Gammage and Holmes, 1975b. There is a drop in the capacity for retaining water in the newly created pores from about 1000 to 100-300  $\mu\text{g}$  of water per  $\text{m}^2$  of newly created surface in passing from fines mildly to severely attacked by water. The severely altered fines of course have a smaller fraction of their pores in the micro-size range.

The concept of adsorbed water etching solar flare and cosmic ray damage tracks has been expounded several times in the past (Holmes et al., 1973a, Gammage et al., 1974a, Gammage et al., 1975b); the present data reinforce these beliefs without offering the much sought after direct proof. The definitive experiment is to adsorb water on to non-porous lunar fines whose damage tracks have been erased at  $1000^\circ\text{C}$  and then reintroduced artificially. The results of such an experiment using  $\text{Fe}^{+9}$  ions of cosmic ray energy will be reported shortly (Holmes et al., 1975).

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#### FIGURE CAPTIONS

Fig. 1. Specific surface areas normalized to the value obtained after outgassing at 25°C prior to treatment with water. Fines 63341: A. after exposure to water vapor at SVP, B. after immersion in aerated liquid water for 30 days, C. after condensing air free, water vapor to soak the fines. Fines 10084: D. after exposure to water vapor at SVP, which was contaminated with 1 torr of air, E. after condensing air free, water vapor to soak the fines.

Fig. 2. Adsorption isotherms of nitrogen at 77°K for the fines 63341 outgassed at 300°C after three types of water treatment. A, B and C signify the aerated liquid water, the air free water vapor, and the air free condensed water treatments, respectively.

Fig. 3. Adsorption isotherms of nitrogen at 77°K measured on fines 63341 outgassed at 25°C, A. after treatment with air free water vapor and B. after treatment with air free condensed water.

Fig. 4. Adsorption isotherms of nitrogen at 77°K measured on the fines 10084 after severe attack by condensed water and subsequent outgassing at either 25 or 300°C to remove the residual water.

Fig. 5. Desorption branches of the isotherms of water vapor at room temperature, measured on fines 74220 after outgassing at 300°C. Each isotherm zero is referred to that weight of fines plus residual water which remained after prolonged evacuation at room temperature.

Fig. 6. Adsorption isotherms of nitrogen, measured at 77°K on fines 74220, after the prior adsorption of water vapor (see Fig. 5) at pressures up to SVP. Holmes' sample was outgassed at 300°C prior to adsorption of nitrogen, Cadenhead's at 150°C.

Table 1. Specific Surface Areas, Accurate to  
+ 0.02 m<sup>2</sup>/g, of a Single Aliquot of  
Fines 10084 Treated in Two Different  
Ways with Water.

Outgassing Temperature (°C)	After the First Treatment with Water Vapor up to SVP plus 1 Torr of Air $\Sigma(\text{m}^2/\text{g})$	After the Second Treatment with Water Vapor Condensed so as to Visibly Moisten the Fines $\Sigma(\text{m}^2/\text{g})$
300 (before any water treatment)	0.59	
25 (after water treatment)	0.54	1.00
100 (after water treatment)	0.54	—
200 (after water treatment)	0.58	—
300 (after water treatment)	0.64	1.24

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Table 2. Specific Surface Areas by Nitrogen Adsorption  
of Apollo 17 Orange Fines 74220 Treated in  
Nearly Identical Manners with Water Vapor

Condition of Fines	Holmes' Data*	Cadenhead's Data <sup>‡</sup> $\Sigma (m^2/g)$
Exposed only briefly to the atmosphere	0.42	0.46 <sup>+</sup>
Outgassed at 300°C and then exposed to water vapor at room temperature and pressures up to SVP.	1.38	0.48

\*Fines outgassed at 300°C prior to adsorbing nitrogen.

<sup>‡</sup>Fines outgassed at 150°C prior to adsorbing nitrogen.

<sup>+</sup>Measured on a different aliquot and reported earlier  
(Cadenhead, 1973)

Table 3. Irreversibly Bound Water on Surfaces Newly Created by Water Treatments in the Absence of Air.

Fines	Treatment	Residual Water at 25°C ( $\mu\text{g}/\text{m}^2$ )
63341	water vapor at pressures up to S.V.P.	865
63341	water vapor condensed so as to visibly moisten the fines	301
10084	water vapor condensed so as to visibly moisten the fines	165

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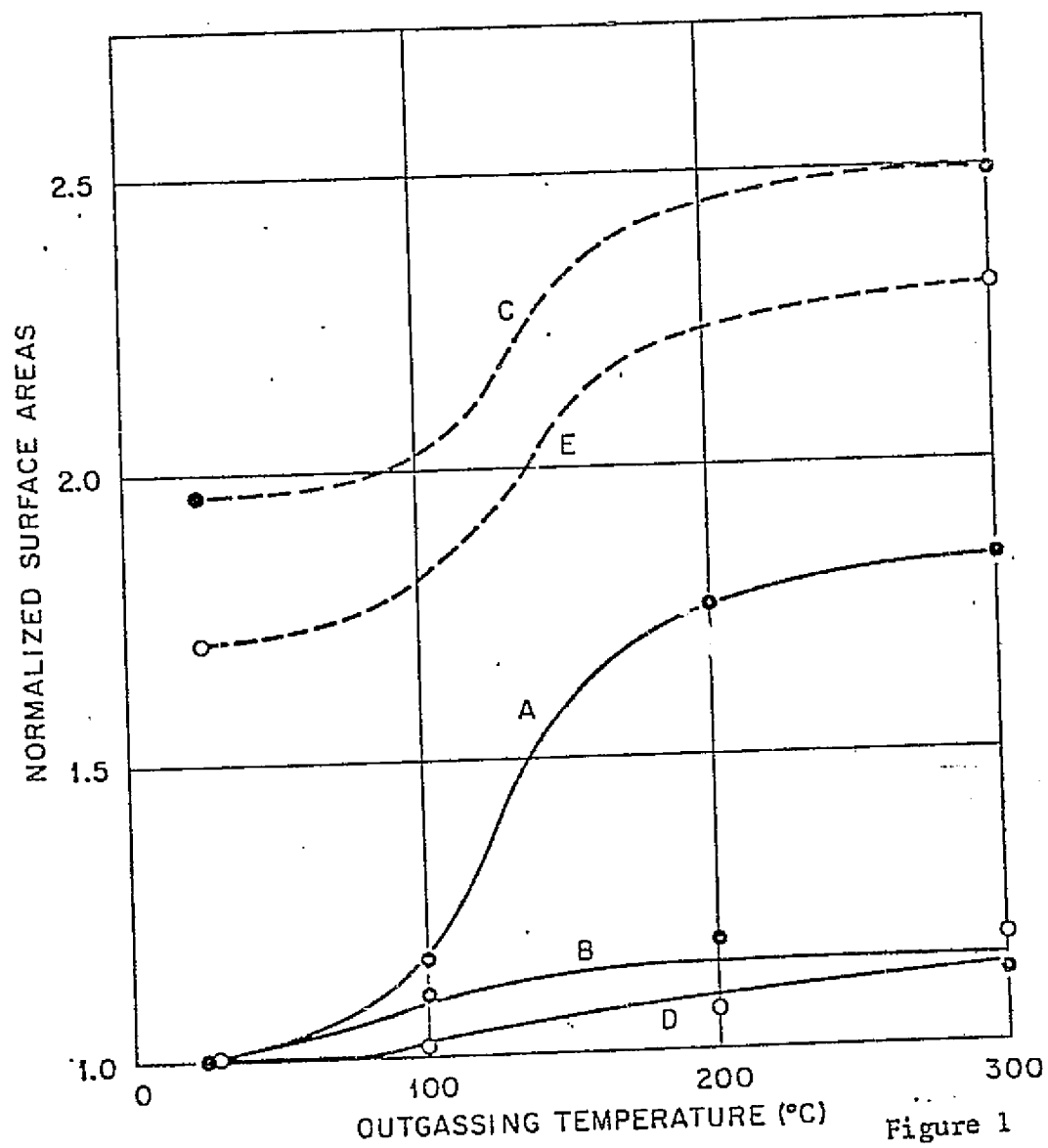
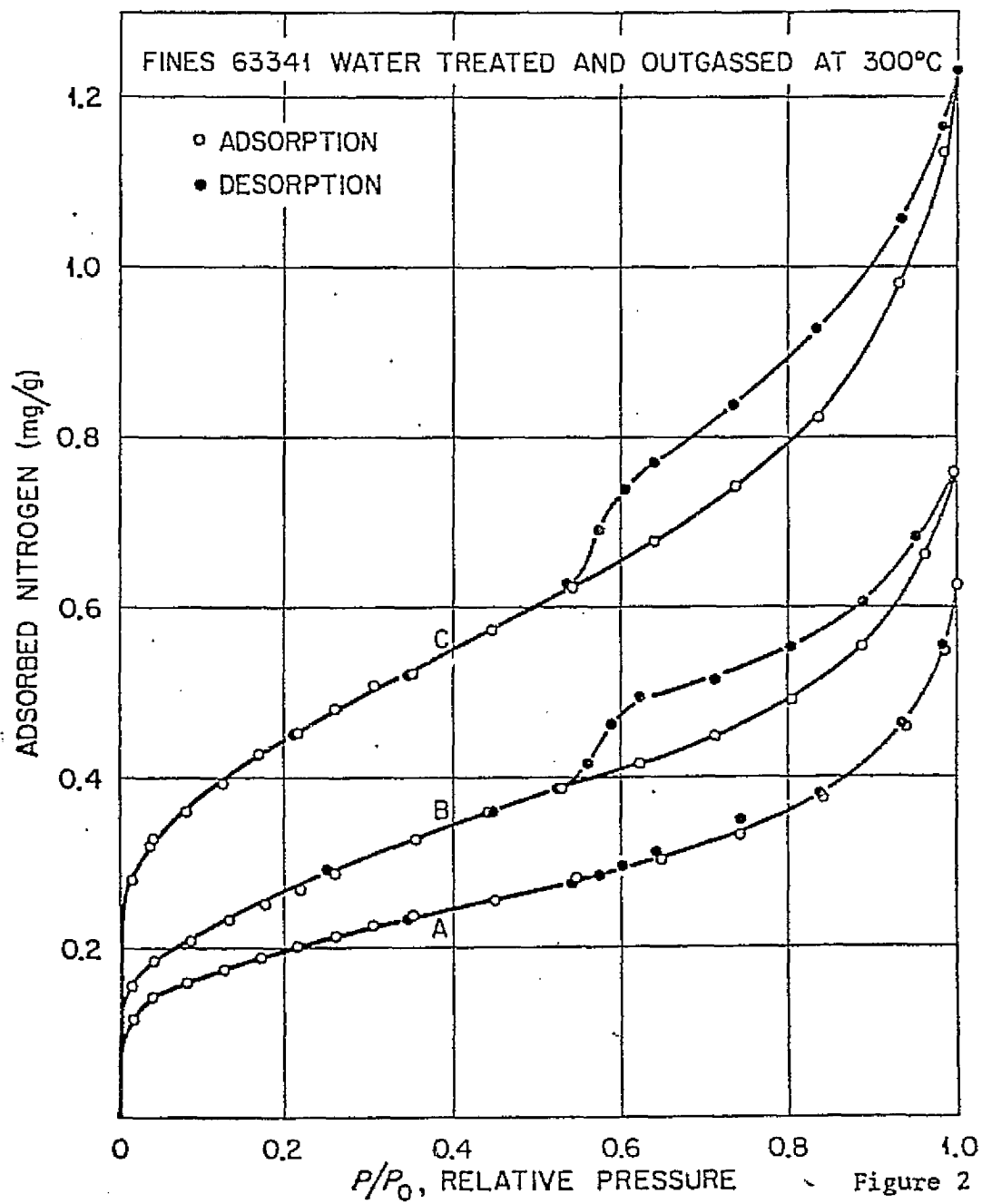


Figure 1



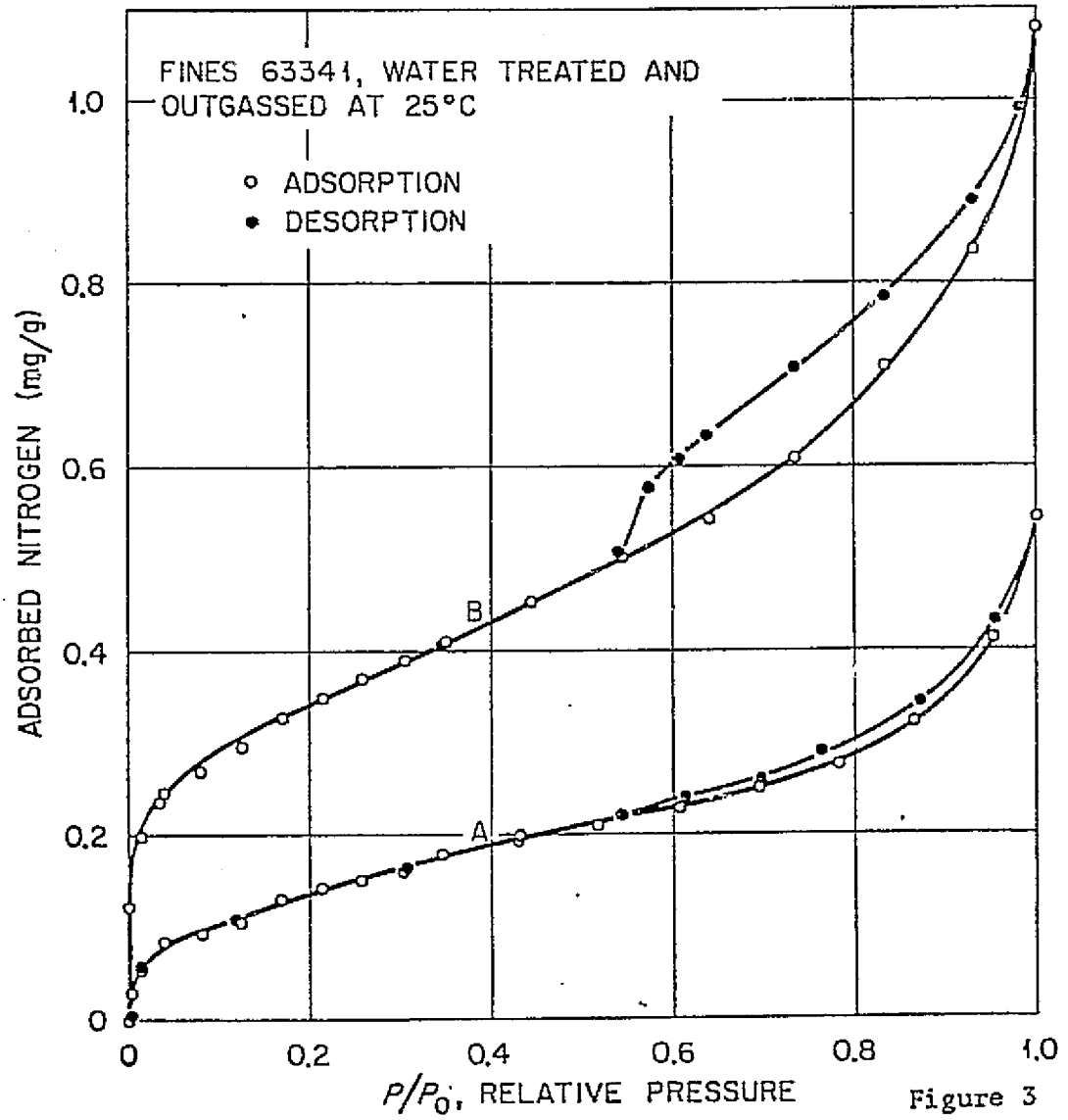


Figure 3

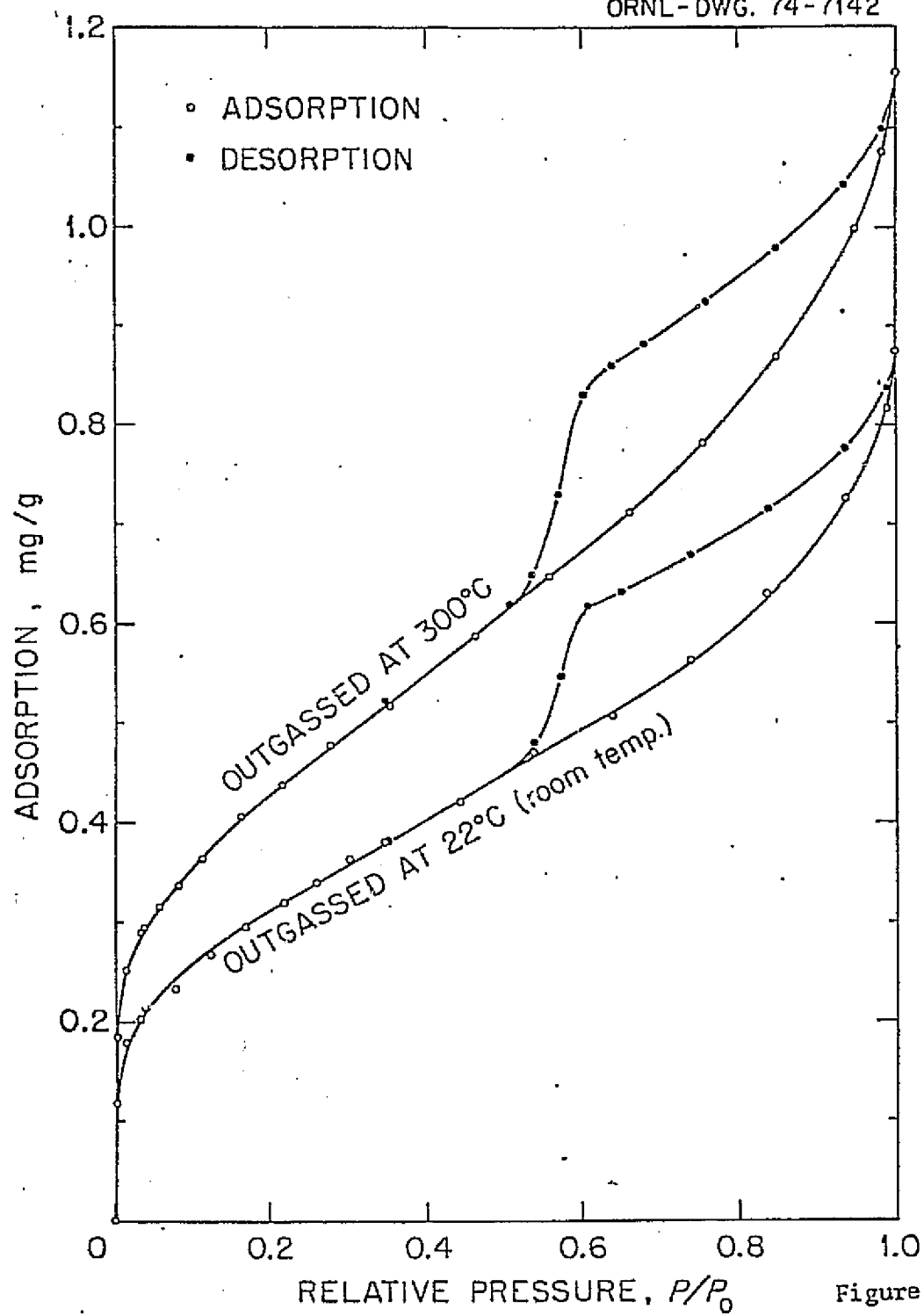


Figure 4



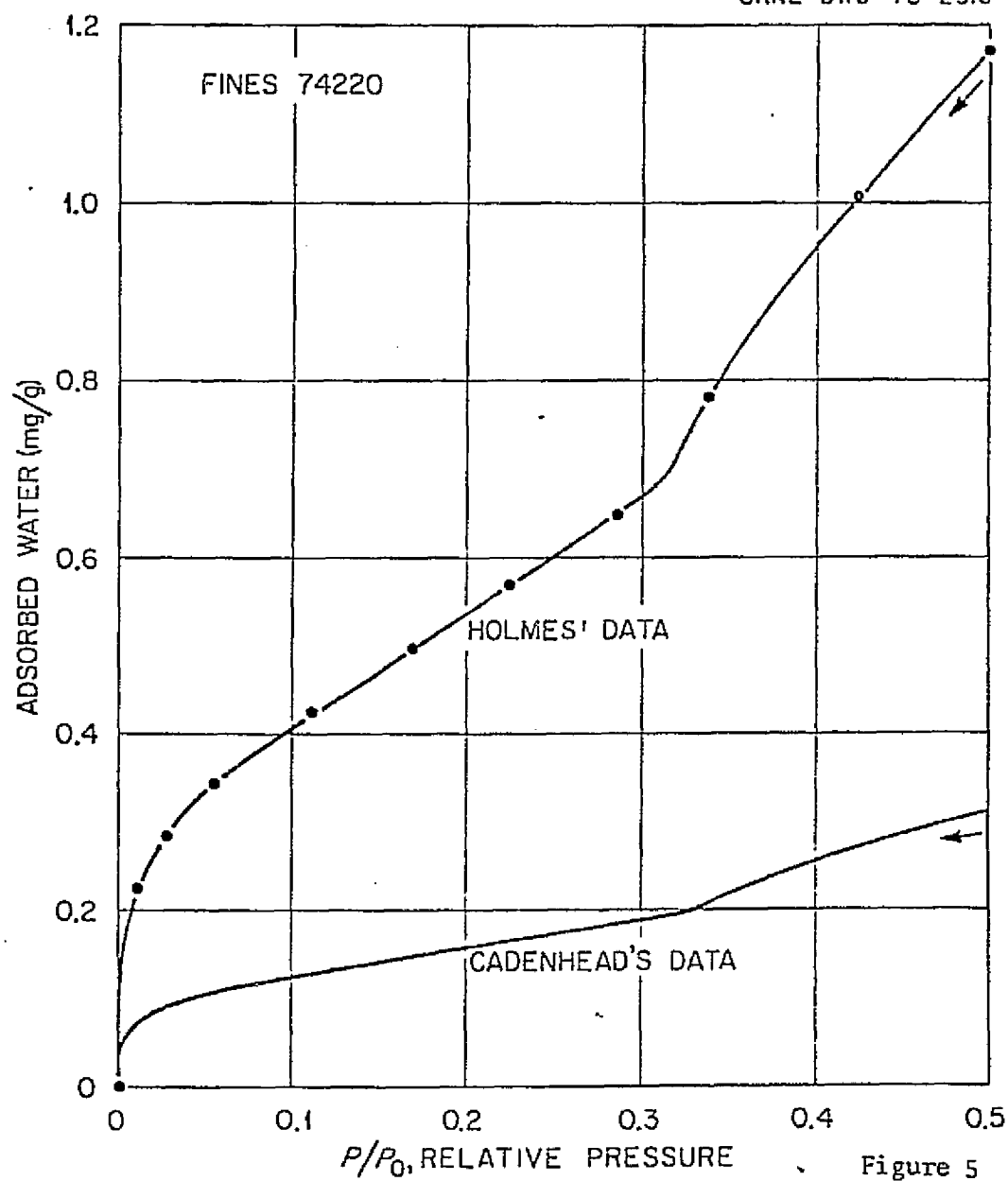


Figure 5

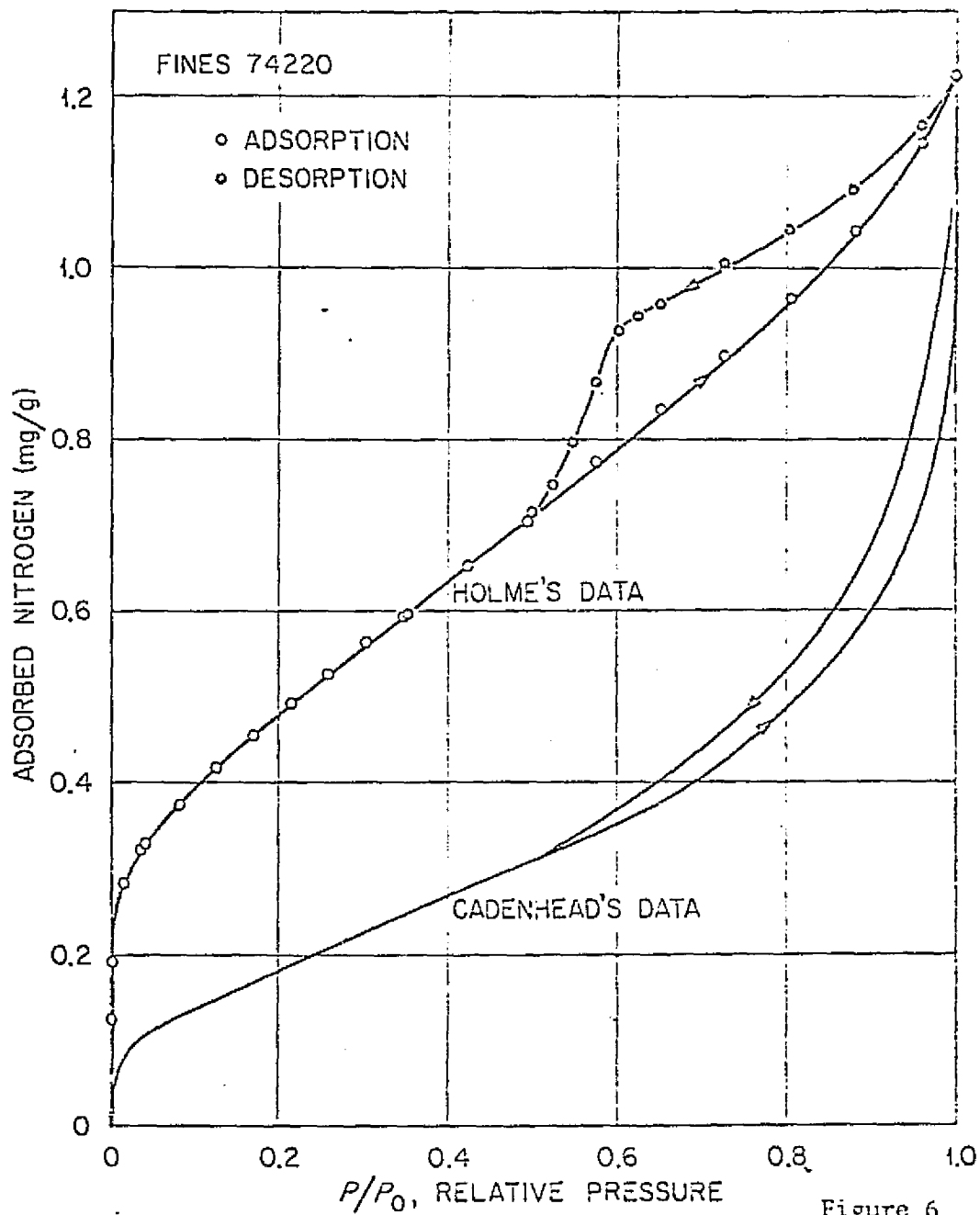


Figure 6